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(54) Title: ACIDIC HARD SURFACE CLEANING COMPOSITIONS

(57) Abstract

Acidic, thickened cleaning compositions which exhibit good long term shelf stability, are particularly effective in the removal of limescale from hard surfaces. The compositions feature surprisingly good viscosity retention over time notwithstanding the presence of formic acid and cellulose based thickeners in the compositions.

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ACIDIC HARD SURFACE CLEANING COMPOSITIONS

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The present invention relates to thickened cleaning and disinfecting compositions which are acidic in nature, and which exhibit good cleaning, and which exhibit long term stability.

While the prior art has provided various compositions directed to cleaning and/or disinfecting hard surfaces, particularly lavatory surfaces, there is yet a continuing need in the art for thickened aqueous compositions which provide: satisfactory cleaning especially of limescale deposits from metal, enamel and porcelain surfaces as found on lavatory fixtures, optionally provide disinfection of treated hard surfaces, and which feature good long term stability of the thickened compositions.

In a first aspect, the present invention provides thickened aqueous acidic hard surface cleaning compositions featuring good storage stability which comprises (in certain preferred embodiments, consists essentially of):

one or more detergents surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 – 10, or where the acid constituent consists solely of formic acid;

a cellulose based thickening composition;

optionally, one or more germicidally active compounds, preferably one or more germicidally active quaternary ammonium compounds;

optionally, one or more conventional additives; and, water.

The inventive aqueous acidic hard surface compositions may further include minor amounts, i.e., less than a combined total amount of 10%wt., preferably not more than 5%wt. of one or more conventional additives including but not limited to: colorants such as pigments and dyes; fragrances and perfumes, pH adjusting agents, germicides such as germicidally active quaternary ammonium compounds, hydrotropes, chelating agents, as well as other conventional additives known to the relevant art.

5 The present invention also provides a method for cleaning (especially the removal of limescale deposits) and disinfecting from hard surfaces, particularly metal, enamel and porcelain surfaces such as those found on lavatory fixtures.

10 According to a second aspect of the invention, there is provided a stable thickened aqueous acidic hard surface cleaning composition which comprises (in certain preferred embodiments, consists essentially of):

15 one or more detergents surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 - 10;

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a cellulose based thickening composition;

optionally a germicidally active compound;

optionally, one or more conventional additives; and,

25 water.

The compositions according to the second aspect of the invention may further include minor amounts, i.e., less than a combined total amount of 10%wt., preferably not more than 5%wt. of conventional additives as noted previously.

According to a third aspect of the invention, there is provided a stable 30 thickened aqueous acidic hard surface cleaning composition which comprises (in certain preferred embodiments, consists essentially of):

one or more detergents surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

an acid constituent comprising formic acid, but most preferably consisting solely of formic acid;

5 a cellulose based thickening composition;

optionally, a germicidally active compound, preferably one or more germicidally active quaternary ammonium compounds;

optionally, one or more conventional additives; and,

water.

10 The compositions according to the third aspect of the invention may further include minor amounts, i.e., less than a combined total amount of 10%wt., preferably not more than 5%wt. of conventional additives as noted previously.

15 The compositions of the invention include one or more detergents surfactants. These may be any suitable anionic, nonionic, amphoteric or zwitterionic compound or composition which provides an effective cleaning benefit to the hard surface being treated. Examples of suitable materials which may be included in the present inventive compositions include those listed by chemical formulas and trade names in described in *McCutcheon's Detergents and Emulsifiers*, North American Edition, 1998; as well as in *Kirk-Othmer, Encyclopedia of Chemical Technology*, 4th Ed., 1997 the relevant contents of which are herein incorporated by reference.

20 Contemplated exemplary useful anionic surfactants include include the water-soluble salts, particularly the alkali metal, ammonium and alkylolammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) These include alkyl sulfates, alkyl sulfonates, alkylether sulfonates, and alkylbenzene sulfonates, each of which may be alkoxylated, especially ethoxylated. By way of example, these include compounds wherein the alkyl or alkylbenzyl group contain from about 6 to about 26 carbon atoms, and which may optionally include to about

12 units of an alkoxy group, (such as ethylene oxides) per molecule. The alkyl groups may be derived from a variety of sources.

Further contemplated as useful anionic surfactants are carboxylates such as alkyl carboxylates, and alkyl polyalkoxycarboxylates.

5 Further useful detergents which may be included one or more nonionic surfactants. Exemplary useful nonionic surfactants include condensation products of alkylene oxide groups with an organic hydrophobic compound, such as an aliphatic or alkyl aromatic compound. Further exemplary useful nonionic surfactants include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides

10

15 Preferred nonionic surfactants include known compounds which may be formed by condensation of an aliphatic or alkyl aromatic compound, with sufficient ethylene oxide to produce a compound having a polyoxyethylene. Preferably the number of ethylene oxide units are present in an amount sufficient to insure solubility of the resulting compound in an aqueous composition of this invention or in any dilution thereof. Desirably, the resulting nonionic surfactants are produced by condensation of about 4-20, more preferably 6-18 moles of ethylene oxide with 1 mole of aliphatic or alkyl aromatic compound.

20

Particularly preferred nonionic surfactants include secondary alcohol ethoxylates. These include compounds which are the condensation products of ethylene oxide groups with a secondary alcohol containing 8 to 20 carbon atoms. These are known, and are commercially available such as in the TERGITOL series of surfactants (ex Union Carbide Co., Danbury, CT.)

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Particularly preferred nonionic surfactants include alkylphenol ethoxylates. These include compounds which are the condensation products of ethylene oxide groups with a alkylphenyl group containing 8 to 20 carbon atoms. These are known, and are commercially available such as in the IGEPAL series of surfactants (ex. Rhodia Inc., Cranbury NJ).

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One preferred class of nonionic surfactants are alkylphenolalkoxylates which include at least one styryl group, i.e., especially tristyrylphenolethoxylates which are commercially available as SOPRAPHOR surfactants (ex. Rhodia Inc.)

Further useful nonionic surfactant compounds include those based on polymeric alkylene oxide block copolymers. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C₂-C₄ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, and can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, thiols and secondary alcohols.

Further useful surfactants which may be included in the inventive compositions are amine oxides. These include alkyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include lauryl, dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide, dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl dimethyl amine oxide. Further amine oxides include alkyl di(hydroxy lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Also contemplated as useful are alkylamidopropyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide.

Contemplated useful amphoteric surfactants include alkylbetaines, amidoalkylbetaines, such as amidopropylbetaines, alkylampho(mono)- and (di)-acetates, alkylampho(mono)- and (di)-propionates, and aminopropionates.

According to certain particularly preferred embodiments the detergents 30 surfactants present consist solely of a nonionic secondary alcohol ethoxylate surfactant, or consist solely of an alkylphenolethoxylate surfactant.

These one or more detergents may be present in any effective amount, but generally these one or more surfactants are present in an amount of up to about 10%wt. Preferably, the detergent surfactant is present in an amount of from about 0.01%wt. to about 10%wt, and most desirably is present in an amount of from about 0.1%wt. to about 8%wt.

An essential feature of the inventive compositions is an acid constituent comprising formic acid. According to the second aspect of the invention, the acid constituent comprises a mixture of formic acid and one or more further water soluble organic acids, particularly those selected from the group consisting of: lactic acid, glycolic acid, and citric acid. According to the second aspect of the invention, it is further particularly preferred that the acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 – 10. According to the third aspect of the invention, the acid constituent may comprise formic acid with a one or more water soluble organic acids, most preferably formic acid is the sole organic acid constituent present.

Desirably, the acid constituent is present in an amount of from 0.001 – 10%wt., more desirably from 0.1 – 10%wt, and most preferably forms from 1 – 5%wt. of the compositions.

The present inventors have surprisingly discovered an apparent synergistic effect from the use of the preferred surfactants in conjunction with formic acid, in the cellulose thickened systems described herein. It has been surprisingly discovered that the long term stability of the cellulose containing compositions is achieved when the formic acid is present with one or more of the preferred surfactants, particularly in the weight ratios described. In the prior art, cellulose thickeners have not been typically used in the presence of formic acid, although formic acid is very desirable as it is particularly effective in removing limescale. However, formic acid has also been known to be incompatible in cellulose thickened systems. According to the present invention, the use of the preferred detergents in conjunction with formic acid substantially reduces the otherwise expected degradation of the cellulose thickener, exemplified by the loss of viscosity of the thickened compositions. The inventive compositions provide good cleaning, especially of limescale stains, and have been found to suffer a

reduced loss of viscosity under the conditions of accelerated aging testing at elevated temperatures, particularly under the test protocol described in the examples. This is particularly important as the compositions are acidic in nature. Particularly preferred surfactants useful in the inventive composition are described in one or more of the Examples.

Preferred embodiments of the inventive compositions feature low odor, are virtually transparent (in the absence of coloring agents) even after high temperature stability testing, and are easy to dispense onto surfaces to be cleaned and disinfected.

As noted, the compositions of the invention are thickened and have a viscosity greater than water. The actual degree of thickening is in part dependent on the amount of thickener included in a composition, as well as on the selection of further components, especially surfactants. Thickeners which may be used are cellulose based thickeners including but not limited to: methyl cellulose, methylethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, and the like. Preferably, the cellulose thickener is one or more of those which are present in the Examples. Generally the thickener is present in not more than about 10%wt. based on the total weight of the composition of which it forms a part. Desirably the thickener is present in an amount of from 0.01 – 5%wt., and more desirably from 0.01 – 2%wt. Starch based thickeners, including so called modified starch based thickeners as frequently encountered in the foods industry are also contemplated as being useful.

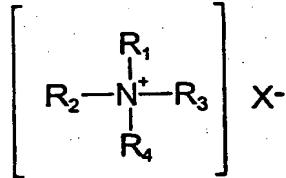
An optional constituent which is nonetheless frequently desirably included is a germicidally active compound. These are compounds or compositions which impart a germicidal effect to the inventive compositions. By way of non-limiting example, these include chloramine, iodine, iodophors such as polyvinyl pyrrolidoneiodine, and chlorhexidine and salts thereof. Suitable salts of chlorhexidine which are soluble in water at ambient temperature to the extent of at least 0.5 percent w/v are, for example, the gluconate, isethionate (2-hydroxyethanesulphonate), formate, acetate, glutamate, succinamate, monodiglycollate, dimethanesulfonate, lactate, di-isobutyrate and glucoheptonate. Other exemplary useful germicidally active compounds include parachloro meta

5 xyleneol, hexachlorophene, 2-bromo-2-nitropropane diol, salicylanilide, didecyl dimethyl ammonium chloride, cetyl dimethylethyl ammonium bromide, alkyl dimethyl benzyl ammonium chloride, alkyl dimethylethyl benzyl ammonium chloride, alkyl dimethylbenzyl ammonium succinate, alkyl dimethyl-3,4-dichlorobenzyl ammonium chloride, 3,3',4',5-tetrachlorosalicylanilide, 3',4',5-trichlorosalicylanilide, 3,5-dibromo-3'-trifluoromethylylsalicylanilide, and 3,4,4'-trichlorocarbamilide. Of course, mixtures of two or more compounds may be used.

10 When present, the germicidally active compound need only be present in germicidally effective amounts, such as in amounts from 0.01% - 10% wt. based on the total weight of the composition of which they form a part. Preferably, these germicidally active compound need be present in reduced amounts such as from about 0.01 – 5%wt., but more preferably from about 0.05 – 3%wt.

15 Contemplated as being particularly useful in providing a germicidal effect are one or more cationic surfactants which provide a broad antibacterial or sanitizing function. Any cationic surfactant which satisfies these requirements may be used and are considered to be within the scope of the present invention, and mixtures of two or more cationic surface active agents, *viz.*, cationic surfactants may also be used. Cationic surfactants are well known, and useful cationic surfactants may be one or more of those described for example in *McCutcheon's Functional Materials, Vol.2, 1998; Kirk-Othmer, Encyclopedia of Chemical Technology*, 4th Ed., Vol. 23, pp. 478-541 (1997), the contents of which are herein incorporated by reference. These are also described in the respective product specifications and literature available from the suppliers of these cationic surfactants.

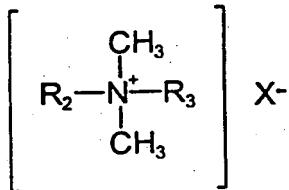
20 Examples of preferred cationic surfactants which provide a germicidal effect to the inventive compositions, include quaternary ammonium compounds which may be characterized by the general structural formula:



where at least one of R₁, R₂, R₃ and R₄ is a alkyl, aryl or alkylaryl substituent of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The alkyl substituents may be long-chain alkyl, long-chain alkoxyaryl, long-chain alkylaryl, halogen-substituted long-chain alkylaryl, long-chain alkylphenoxyalkyl, arylalkyl, etc. The remaining substituents on the nitrogen atoms other than the abovementioned alkyl substituents are hydrocarbons usually containing no more than 12 carbon atoms. The substituents R₁, R₂, R₃ and R₄ may be straight-chained or may be branched, but are preferably straight-chained, and may include one or more amide, ether or ester linkages. The counterion X may be any salt-forming anion which permits water solubility of the quaternary ammonium complex.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide, ether or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are found useful in the practice of the present invention include those which have the structural formula:



wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl, or R₂ is C₁₂₋₁₆alkyl, C₈₋₁₈alkylethoxy, C₈₋₁₈alkylphenolethoxy and R₃ is benzyl, and X is a halide, for example chloride, bromide or iodide, or is a methosulfate anion. The alkyl groups recited in R₂ and R₃ may be straight-chained or branched, but are preferably substantially linear.

Particularly useful quaternary germicides include compositions which include a single quaternary compound, as well as mixtures of two or more different quaternary compounds. Such useful quaternary compounds are available under the BARDAC®, BARQUAT®, HYAMINE®, LONZABAC®, and ONYXIDE® trademarks, which are more fully described in, for example, *McCutcheon's Functional Materials* (Vol. 2), North American Edition, 1998, as well as the respective product literature from the suppliers identified below. For example, BARDAC® 205M is described to be a liquid containing alkyl dimethyl benzyl ammonium chloride, octyl decyl dimethyl ammonium chloride; didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 80% active (BARDAC® 208M)); described generally in *McCutcheon's* as a combination of alkyl dimethyl benzyl ammonium chloride and dialkyl dimethyl ammonium chloride); BARDAC® 2050 is described to be a combination of octyl decyl dimethyl ammonium chloride/didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (also available as 80% active (BARDAC® 2080)); BARDAC® 2250 is described to be didecyl dimethyl ammonium chloride (50% active); BARDAC® LF (or BARDAC® LF-80), described as being based on dioctyl dimethyl ammonium chloride (BARQUAT® MB-50, MX-50, OJ-50 (each 50% liquid) and MB-80 or MX-80 (each 80% liquid) are each described as an alkyl dimethyl benzyl ammonium chloride; BARDAC® 4250 and BARQUAT® 4250Z (each 50% active) or BARQUAT® 4280 and BARQUAT 4280Z (each 80% active) are each described as alkyl dimethyl benzyl ammonium chloride/alkyl dimethyl ethyl

benzyl ammonium chloride. Also, HYAMINE® 1622, described as diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride (50% solution); HYAMINE® 3500 (50% actives), described as alkyl dimethyl benzyl ammonium chloride (also available as 80% active (HYAMINE® 3500-80)); and HYMAINE® 2389 described as being based on methyldodecylbenzyl ammonium chloride and/or methyldodecylxylene-bis-trimethyl ammonium chloride. (BARDAC®, BARQUAT® and HYAMINE® are presently commercially available from Lonza, Inc., Fairlawn, New Jersey). BTC® 50 NF (or BTC® 65 NF) is described to be alkyl dimethyl benzyl ammonium chloride (50% active); BTC® 99 is described as didecyl dimethyl ammonium chloride (50% active); BTC® 776 is described to be myrisalkonium chloride (50% active); BTC® 818 is described as being octyl decyl dimethyl ammonium chloride, didecyl dimethyl ammonium chloride, and dioctyl dimethyl ammonium chloride (50% active) (available also as 80% active (BTC® 818-80%)); BTC® 824 and BTC® 835 are each described as being of alkyl dimethyl benzyl ammonium chloride (each 50% active); BTC® 885 is described as a combination of BTC® 835 and BTC® 818 (50% active) (available also as 80% active (BTC® 888)); BTC® 1010 is described as didecyl dimethyl ammonium chloride (50% active) (also available as 80% active (BTC® 1010-80)); BTC® 2125 (or BTC® 2125 M) is described as alkyl dimethyl benzyl ammonium chloride and alkyl dimethyl ethylbenzyl ammonium chloride (each 50% active) (also available as 80% active (BTC® 2125 80 or BTC® 2125 M)); BTC® 2565 is described as alkyl dimethyl benzyl ammonium chlorides (50% active) (also available as 80% active (BTC® 2568)); BTC® 8248 (or BTC® 8358) is described as alkyl dimethyl benzyl ammonium chloride (80% active) (also available as 90% active (BTC® 8249)); ONYXIDE® 3300 is described as n-alkyl dimethyl benzyl ammonium saccharinate (95% active). (BTC® and ONYXIDE® are presently commercially available from Stepan Company, Northfield, Illinois.) Polymeric quaternary ammonium salts based on these monomeric structures are also considered desirable for the present invention. One example is POLYQUAT®, described as being a 2-butenyldimethyl ammonium chloride polymer.

In compositions according to the invention, when present, the quaternary ammonium compound is most desirably present in sufficient amounts which are

effective in exhibiting satisfactory germicidal activity against selected bacteria sought to be treated. The quaternary ammonium compound need only be present in germicidally effective amounts, such as in amounts from 0.01% - 10% wt. based on the total weight of the composition of which they form a part. Generally, 5 effective "hospital strength" germicidal efficacy meeting current EPA guidelines is provided when the quaternary ammonium compounds are present in an amount of from about 0.05%wt. to about 5 %wt. When present, the quaternary ammonium compound is desirably present in an amount of from 0.05%wt. to about 3%wt, based on the total weight of the inventive compositions being taught herein.

10 According to certain preferred embodiments, one or more quaternary ammonium compounds are present to the exclusion of other germicidally active compounds.

The compositions of the invention are acidic, and exhibit a pH of less than 7, more preferably about 5 and less and most preferably a pH from 3 to 4.5.

15 Whereas the presence of the acid mixture described above will impart acidity to the composition, it may be desirable to include a buffer or pH adjusting agent to the compositions to maintain the compositions approximately at a desired pH (or pH range). Exemplary useful pH buffers include inorganic and organic buffering agents, and especially include alkali metal and alkaline earth metal hydroxides such as sodium hydroxide and potassium hydroxide. Others not 20 described here may also be used. Particularly preferred is sodium hydroxide which is widely available at low cost, and is effective.

For any particular composition described above, any optional ingredients should be compatible with the other ingredients present.

25 The inventive compositions do not include bleach such as chlorine bleach, a bleach releasing compound such as a halohydantoin, nor do they include hydrogen peroxide.

30 As is noted above, the compositions according to the invention are aqueous in nature. Water is added to order to provide to 100% by weight of the compositions of the invention. The water may be tap water, but is preferably distilled and is most preferably deionized water.

According to certain preferred embodiments of the first aspect of the invention there are provided thickened aqueous acidic hard surface cleaning and disinfecting compositions which comprise (preferably, consist essentially of):

- 5 0.1 – 10%wt. one or more deterotive surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
- 10 0.1 – 10%wt. an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 – 10, or where the acid constituent consists solely of formic acid;
- 15 0 - 5%wt., preferably about 0.01 – 5%wt., of one or more germicidally active compounds, especially preferably one or more germicidally active quaternary ammonium compounds;
- 20 0.01 – 5%wt. of a cellulose based thickening composition; optionally up to 10%wt. of one or more optional constituents; with the remaining balance to 100%wt. of water; wherein the compositions are at an acidic pH, preferably at a pH in the range of 3 – 4.5.

The inventive compositions may include minor amounts as indicated above, but preferably not more than about 5%wt. of one or more optional including, but not limited to, non-aqueous solvents, pH buffering agents, pH adjusting agents, perfumes, perfume carriers, optical brighteners, colorants, hydrotropes.

25 According to certain preferred embodiments of the second aspect of the invention there are provided thickened aqueous acidic hard surface cleaning and disinfecting compositions which comprise (preferably, consist essentially of):

- 30 0.1 – 10%wt. of one or more deterotive surfactants selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
- 0.1 – 10%wt. of an acid constituent comprising an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting

of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 - 100

5 0 - 5%wt., preferably about 0.01 - 5%wt., of a germicidally active compound, especially preferably a one or more quaternary ammonium compounds;

10 0.01 - 5%wt. a cellulose based thickening composition; optionally up to 10%wt. of one or more optional constituents; with the remaining balance to 100%wt. of water;

wherein the compositions are at an acidic pH, preferably at a pH in the range of 3 - 4.5.

15 The inventive compositions may include minor amounts as indicated above, but preferably not more than about 5%wt. of one or more optional including, but not limited to, non-aqueous solvents, pH buffering agents, pH adjusting agents, perfumes, perfume carriers, optical brighteners, colorants, hydrotropes.

According to certain preferred embodiments of the third aspect of the invention there are provided thickened aqueous acidic hard surface cleaning and disinfecting compositions which comprise (preferably, consist essentially of):

20 0.1 - 10%wt. of one or more deterotive surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

0.1 - 10%wt. of an acid constituent comprising formic acid, but most preferably consisting solely of formic acid;

0.01 - 5%wt. of a cellulose based thickening composition;

25 0 - 5%wt., preferably about 0.01 - 5%wt., of a germicidally active compound, especially preferably one or more quaternary ammonium compounds;

optionally up to 10%wt. of one or more optional constituents; with the remaining balance to 100%wt. of water;

30 wherein the compositions are at an acidic pH, preferably at a pH in the range of 3 - 4.5.

The inventive compositions may include minor amounts as indicated above, but preferably not more than about 5%wt. of one or more optional including, but not limited to, non-aqueous solvents, pH buffering agents, pH adjusting agents, perfumes, perfume carriers, optical brighteners, colorants, hydrotropes.

5 By way of non-limiting example exemplary pH adjusting agents include phosphorus containing compounds, monovalent and polyvalent salts such as of silicates, carbonates, and borates, certain acids and bases, tartrates and certain acetates. Further exemplary pH adjusting agents include mineral acids, basic compositions, and organic acids, which are typically required in only minor amounts. By way of further non-limiting example pH buffering compositions include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as pH buffers. It may also be suitable to use as pH buffers materials such as aluminosilicates (zeolites), borates, alumina and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. Citrates, and citric acid may also be advantageously used in the compositions.

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20 The thickened aqueous acidic hard surface cleaning and disinfecting compositions according to the invention are desirably provided as a ready to use product which may be directly applied to a hard surface. The inventive compositions are particularly useful in cleaning and disinfecting lavatory fixtures such as shower stalls, bathtubs and bathing appliances (racks, curtains, shower doors, shower bars) toilets, bidets, wall and flooring surfaces especially those which include refractory materials and the like. Especially the inventive compositions are useful in the cleaning and disinfecting of lavatory fixtures, especially toilets and bidets. They may be packaged in any suitable container particularly flasks or bottles, including squeeze-type bottles, as well as bottles provided with a spray apparatus which is used to dispense the composition by spraying.

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The present invention also provides a method for cleaning a hard surface, particularly for cleaning lavatory surfaces especially wherein limescale is prone to occur, i.e., toilets, bidets, etc.

5 The compositions according to the invention, including certain particularly preferred embodiments of the invention and certain particularly preferred detergents and surfactants are presented in the following examples.

Examples:

A number of formulations according to the invention (indicated as Examples, "E") were produced. Each of these were made by mixing the constituents outlined on Table 1A by adding the individual constituents into a beaker of deionized water at room temperature (68°F, 20°C) which was stirred with a conventional magnetic stirring rod. Stirring continued until the formulation was homogenous in appearance. It is to be noted that the constituents might be added in any order, but it is preferred that water be the initial constituent provided to a mixing vessel or apparatus as it is the major constituent and addition of the further constituents thereto is convenient. Also, it is convenient to disperse the cellulose thickener into a premixture with a quantity of water, and to add this premixture to the beaker. The exact compositions of the example formulations are listed on 15 Table 1A, below.

20

Table 1A

	E1	E2	E3	E4	E5	E6	E7
nonylphenolethoxylate	0.5	--	--	--	0.5	--	--
secondary alcohol ethoxylate	--	0.5	--	--	--	--	--
tristyrylphenol ethoxylate	--	--	--	0.5	--	--	--
sodium alkyl benzene sulfonate (38%)	--	--	--	--	1.5	--	2.0
lauramine oxide (30%)	--	--	0.5	--	--	--	--
oleamidopropyl betaine (35%)	--	--	--	--	--	0.5	--
formic acid (94%)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
quaternary ammonium chloride (80%)	1.5	1.5	1.5	1.5	--	1.5	--
hydroxyethyl cellulose	0.5	0.5	0.5	0.5	0.5	0.5	0.5
sodium hydroxide (50%)	--	--	1.15	1.15	1.15	1.15	1.15
fragrance and dye	0.35	0.35	0.4	0.4	0.4	0.4	0.4
di water	to 100						
initial pH	4.0	4.0	4.0	4.0	4.0	4.0	4.0

5

It is to be understood that the amounts of the constituents are listed above based on the active weights of the respective material, assuming 100%wt. active, which may however have been supplied as less than 100%wt. actives. The identity of the individual constituents described in Table 1A above, their percentage by weight 'actives', as well as presently available commercial sources, are described in more detail in Table 2A, below.

Table 2A

nonylphenolethoxylate	nonylphenolethoxylate, supplied as IGEPAL CO-730 from Rhodia Inc. (Cranbury, NJ)
secondary alcohol ethoxylate	secondary alcohol ethoxylate supplied as TERGITOL 15-S-9 from Union Carbide Co. (Danbury, CT)
tristyrylphenol ethoxylate	tristyrylphenol ethoxylate supplied as SOPROPHOR BSU (from Rhodia Inc., Cranbury NJ)
sodium alkyl benzene sulfonate (38%)	sodium alkyl benzene sulfonate supplied as BIOSOFT D-40 (38%wt. actives) from Stepan Co., Northfield IL
lauramine oxide (30%)	lauramine oxide, supplied as AMMONYX LO (30%wt. actives), from Stepan Co., Northfield IL
oleamidopropyl betaine (35%)	, supplied as MACKAM HV (35%), from the McIntyre Group
quaternary ammonium chloride (80%)	mixture of alkyl dimethyl benzyl ammonium chloride, octyl-decyl-, dioctyl- and didecyl- dimethyl ammonium chlorides (80%wt. actives, 10%wt. ethanol, 10%wt. water)
hydroxyethyl cellulose	hydroxyethyl cellulose (100 %wt. actives) from Union Carbide Co. (Danbury, CT)
fragrance and dye	proprietary compositions of their respective manufacturers
di water	deionized water

Further formulations according to the invention (indicated as Examples, "E") were produced generally according to the protocol described previously with reference to the formulations of Table 1A are described on Table 1B, below.

5

Table 1B

	E8	E9	E10
alcohol ethoxylate	—	0.5	—
sodium alkyl benzene sulfonate (38%)	—	1.0	—
lauramine oxide (30%)	1.0	—	—
oleamidopropyl betaine (35%)	—	—	1.0
quaternary ammonium chloride (80%)	1.5	—	1.5
formic acid (94%)	1.1	1.1	1.1
glycolic acid (70%)	1.4	1.4	1.4
hydroxyethyl cellulose	0.5	0.5	0.5
fragrance and dye	0.4	0.4	0.4
di water	to 100	to 100	to 100

10

Again, It is to be understood that the amounts of the constituents are listed above based on the active weights of the respective material, assuming 100%wt. active, which may however have been supplied as less than 100%wt. actives. The identity of the individual constituents described in Table 1B above, their

percentage by weight 'actives', as well as presently available commercial sources, are described in more detail in Table 2B, below.

Table 2B

alcohol ethoxylate	linear C ₁₂ -C ₁₆ alcohol ethoxylate, with an average of 7.3 ethylene oxide groups per molecule, supplied as GENAPOL 26-L-60, from Clariant Inc., Muttenz, Switzerland
sodium alkyl benzene sulfonate (38%)	sodium alkyl benzene sulfonate, supplied as BIOSOFT D-40 (38%wt. actives), from Stepan Co.
lauramine oxide (30%)	lauramine oxide, supplied as AMMONYX LO (30%wt. actives, Stepan Co.)
oleamidopropyl betaine (35%)	oleamidopropyl betaine, supplied as MACKAM HV (35%wt. actives), from the McIntyre Group
quaternary ammonium chloride (80%)	mixture of alkyl dimethyl benzyl ammonium chloride, octyl-decyl-, dioctyl- and didecyl- dimethyl ammonium chlorides (80%wt. actives, 10%wt. ethanol, 10%wt. water)
formic acid (94%)	formic acid, from BASF (94%wt. actives)
glycolic acid (70%)	glycolic acid, from E.I. DuPont Co. (70%wt. actives)
hydroxyethyl cellulose	hydroxyethyl cellulose supplied as CELLOSIZE QP-100MH (100%wt.actives) from Union Carbide Co. (Danbury, CT)
fragrance and dye	proprietary compositions of their respective manufacturers
di water	deionized water

For purposes of comparison, comparative formulations (indicated as Comparative Examples, "E") described on Table 1C were produced generally according to the protocol described previously with reference to the formulations of Table 1A.

Table 1C

	C1	C2	C3
linear primary alcohol ethoxylate	0.5	0.5	0.5
quaternary ammonium chloride (80%)	1.1	1.1	1.1
citric acid	2.5	—	2.5
glycolic acid (70%)	—	1.43	—
hydroxyethyl cellulose	0.5	0.5	0.5
fragrance and dye	0.35	0.35	0.35
di water	to 100	to 100	to 100
initial pH	3.52	3.52	4.05

The identity of the individual constituents described in Table 1C above, their percentage by weight 'actives', as well as presently available commercial sources, are described in more detail in Table 2C, below.

Table 2C

linear alcohol ethoxylate	supplied by GENAPOL 26-L-60, a linear C ₁₂ -C ₁₆ alcohol ethoxylate, with an average of 7.3 ethylene oxide groups per molecule (100%wt. actives)
quaternary ammonium chlorides	supplied by BTC-888 (Stepan Chem. Co.) a blend of dialkyl dimethyl benzyl ammonium chloride, and alkyl dimethyl benzyl ammonium chloride (80%wt. actives) which includes 10%wt. ethanol
hydroxyethyl cellulose	supplied by CELLOSIZE QP-100MH from Union Carbide Co. (Danbury, CT) (100%wt. actives)
formic acid	supplied in an aqueous, technical grade, Aldrich Co. or other supplier (94%wt. actives)
citric acid	supplied in an aqueous, technical grade, Aldrich Co. or other supplier (100%wt. actives)
glycolic acid	supplied in an aqueous, technical grade, Aldrich Co. or other supplier (57%wt. actives)
fragrance and dye	proprietary compositions of their respective manufacturers
di water	deionized water

Evaluation of Shelf Stability:

Formulations according to the invention as described on Tables 1A and 1B were evaluated in order to determine their initial viscosity. Formulations were placed in sealed glass containers, and subjected to an accelerated aging test wherein the formulations were maintained at 120°F (48.5°C) for a period of 6 weeks. At periodic intervals, aliquots of each formulation were taken and used to determine the viscosity in the manner outlined above. All viscosity measurements were performed on aliquots of tested formulation using a Brookfield Viscometer, fitted with a LV-2 spindle at a rotational speed of 60 rpm at 22°C. Viscosity measurement results are reported in centipoise and are reported on Table 3, below. Subsequent to this accelerated aging test, all of the formulations were observed to each be a colored, substantially transparent single phase mixture with good flow properties; bulk phase separation was not observed to occur.

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Table 3

Formulation:	Initial Viscosity, cps	Cumulative % Viscosity loss at week 1	Cumulative % Viscosity loss at week 2	Cumulative % Viscosity loss at week 3	Cumulative % Viscosity loss at week 4	Cumulative % Viscosity loss at week 5	Cumulative % Viscosity loss at week 6
E1	394.0	12.69%	15.99%	NT	18.27%	NT	27.41%
E2	384.0	16.15%	16.93%	NT	21.35%	NT	27.34%
C1	417.0	19.90%	32.37%	36.69%	49.64%	58.03%	64.03%
C2	438.0	16.89%	21.92%	23.34%	31.05%	37.90%	39.04%
C3	417.0	13.19%	18.23%	24.22%	29.98%	34.77%	42.45%

'NT' indicates that the sample was not tested that week

As can be seen from the results indicated on Table 3, the compositions of the invention particularly as exemplified by the Examples demonstrate surprising viscosity stability. As also can be seen from the examples, compositions which included citric or glycolic acid in the absence of formic acid exhibited substantial cumulative viscosity losses during the accelerated aging test.

Claims:

- 5 1. A thickened aqueous acidic hard surface cleaning composition which comprises:
 - one or more detergentsurfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
 - an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 – 10, or
 - 15 where the acid constituent consists solely of formic acid;
 - a cellulose based thickening composition;
 - optionally, one or more germicidally active compounds, preferably one or more germicidally active quaternary ammonium compounds;
 - optionally, one or more conventional additives;
 - 20 and, water.
2. A composition according to claim 1 wherein the detergentsurfactant consists solely of a nonionic secondary alcohol ethoxylate surfactant.
- 25 3. A composition according to claim 1 wherein the detergentsurfactant consists solely of an alkylphenolethoxylate.
4. A composition according to claim 1 which comprises:
 - 0.1 – 10%wt. one or more detergentsurfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
 - 30 0.1 – 10%wt. an acid constituent comprising formic acid and one or more water soluble organic acids, particularly water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and particularly where the acid mixture include formic acid and at least

one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 – 10, or where the acid constituent consists solely of formic acid;

5 0 - 5%wt. of one or more germicidally active compounds, most preferably one or more germicidally active quaternary ammonium compounds;

10 0.01 – 5%wt. of a cellulose based thickening composition; optionally up to 10%wt. of one or more optional constituents; with the remaining balance to 100%wt. of water; wherein the compositions are at an acidic pH, preferably at a pH in the range of from 3 to 4.5.

15 5. A composition according to any of claims 1 - 4 wherein the composition includes one or more germicidally active compounds.

6. A composition according to claim 5 wherein the composition includes a quaternary ammonium compound.

20 7. A composition according to claim 1 which comprises :
one or more deterutive surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

25 an acid constituent comprising formic acid and one or more water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid;

a cellulose based thickening composition;
optionally a germicidally active compound;
optionally, one or more conventional additives; and,
water.

30 8. A composition according to claim 7 wherein the acid mixtures include formic acid and at least one other water soluble organic acid and wherein

these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 - 10;

9. A composition according to any of claims 7 - 8 wherein the composition includes one or more germicidally active compounds.

5 10. A composition according to claim 9 wherein the composition includes a quaternary ammonium compound.

10 11. A composition according to claim 1 wherein the deterotive surfactant comprises a nonionic secondary alcohol ethoxylate surfactant and an alkylphenolethoxylate surfactant.

12. A composition according to claim 7 which comprises:

15 0.1 - 10%wt. of one or more deterotive surfactants selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

20 0.1 - 10%wt. of an acid constituent comprising an acid constituent comprising formic acid and one or more water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 - 100

25 0.05 - 5%wt. of a germicidally active quaternary ammonium compound;

0.01 - 5%wt. a cellulose based thickening composition;

optionally up to 10%wt. of one or more optional constituents; with the remaining balance to 100%wt. of water;

wherein the compositions are at a pH in the range of 3 - 4.5.

30 13. A composition according to claim 12 which consists essentially of:

- 0.1 – 10%wt. of one or more deterotive surfactants selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
- 5 0.1 – 10%wt. of an acid constituent comprising an acid constituent comprising formic acid and one or more water soluble organic acids selected from the group consisting of: lactic acid, glycolic acid and citric acid and where the acid mixture include formic acid and at least one other water soluble organic acid where wherein these acids are present in a weight ratio of formic acid:water soluble organic acids of 1:0.1 - 100
- 10 0.05 - 5%wt. of a germicidally active quaternary ammonium compound;
- 0.01 – 5%wt. a cellulose based thickening composition;
- 0 - 10%wt. of one or more optional constituents;
- with the remaining balance to 100%wt. of water;
- wherein the compositions are at a pH in the range of 3 – 4.5.
- 15 14. A composition according to claim 1 which comprises:
- one or more deterotive surfactants, selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
- an acid constituent consisting solely of formic acid;
- 20 a cellulose based thickening composition;
- optionally, a germicidally active compound, preferably one or more germicidally active quaternary ammonium compounds;
- optionally, one or more conventional additives; and,
- and, water.
- 25 15. A composition according to claim 14 wherein the composition includes one or more germicidally active compounds.
16. A composition according to claim 15 wherein the composition includes a quaternary ammonium compound.
- 30 17. A composition according to claim 14 which comprises:

0.1 – 10%wt. a detergentsurfactant which comprises one or more detergentsurfactants, selected from selected from anionic, nonionic, amphoteric or zwitterionic surfactants;

0.1 – 10%wt. an acid constituent consisting solely of formic acid;

5 0.05 – 5%wt. of a germicidally active a quaternary ammonium compound;

0.01 – 5%wt. a cellulose based thickening composition;

0 - 10%wt. of one or more optional constituents;

10 with the remaining balance to 100%wt. of water;

wherein the constituents are at an acidic pH, preferably a pH in the range of 3 – 4.5.

18. A composition according to claim 17 which consists essentially of:
- 0.1 – 10%wt. a detergentsurfactant which comprises one or more detergentsurfactants, selected from selected from anionic, nonionic, amphoteric or zwitterionic surfactants;
- 0.1 – 10%wt. an acid constituent consisting solely of formic acid;
- 15 0.05 – 5%wt. of a germicidally active a quaternary ammonium compound;
- 0.01 – 5%wt. a cellulose based thickening composition;
- 0 - 10%wt. of one or more optional constituents;
- 20 with the remaining balance to 100%wt. of water;
- wherein the constituents are at an acidic pH, preferably a pH in the range of 3 – 4.5.
- 25
19. A process for cleaning limescale from a hard surface which comprises the process step of:
- contacting the hard surface having limescale thereon with a cleaning effective amount of the composition according to any preceding 30 claim to clean limescale present therefrom.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02949

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D11/00 C11D3/20 C11D3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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P,X	WO 99 16854 A (RECKITT & COLMAN) 8 April 1999 (1999-04-08) claims 1-4,6-10	1,4-10, 12,19
A	claims 1,7-9	14-18
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Inter. Application No.
PCT/GB 99/02949

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